

Alumoåkermanite, $(\text{Ca},\text{Na})_2(\text{Al},\text{Mg},\text{Fe}^{2+})(\text{Si}_2\text{O}_7)$, a new mineral from the active carbonatite-nephelinite-phonolite volcano Oldoinyo Lengai, northern Tanzania

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Alumoåkermanite, $(\text{CaNa})_2(\text{Al},\text{Mg},\text{Fe}^{2+})(\text{Si}_2\text{O}_7)$, is a new mineral member of the melilite group from the active carbonatite-nephelinite-phonolite volcano Oldoinyo Lengai, Tanzania. The mineral occurs as tabular phenocrysts and microphenocrysts in melilite-nephelinitic ashes and lapilli-tuffs. Alumoåkermanite is light brown in colour; it is transparent, with a vitreous lustre and the streak is white. Cleavages or partings are not observed. The mineral is brittle with an uneven fracture. The measured density is $2.96(2) \text{ g/cm}^3$. The Mohs hardness is $\sim 4.5\text{--}6$. Alumoåkermanite is uniaxial (–) with $\omega = 1.635(1)$ and $\epsilon = 1.624\text{--}1.626(1)$. In a $30 \mu\text{m}$ thin section (+N), the mineral has a yellow to orange interference colour, straight extinction and positive elongation, and is nonpleochroic. The average chemical formula of the mineral derived from electron microprobe analyses is: $(\text{Ca}_{1.48}\text{Na}_{0.50}\text{Sr}_{0.02}\text{K}_{0.01})_{\Sigma 2.01}(\text{Al}_{0.44}\text{Mg}_{0.30}\text{Fe}_{0.17}^{2+}\text{Fe}_{0.07}^{3+}\text{Mn}_{0.01})_{\Sigma 0.99}(\text{Si}_{1.99}\text{Al}_{0.01}\text{O}_7)$. Alumoåkermanite is tetragonal, space group $P4_2/m$ with $a = 7.7661(4) \text{ \AA}$, $c = 5.0297(4) \text{ \AA}$, $V = 303.4(1) \text{ \AA}^3$ and $Z = 2$. The five strongest powder-diffraction lines [d in \AA , (I/I_0), hkl] are: 3.712, (13), (111); 3.075, (25), (201); 2.859, (100), (211); 2.456, (32), (311); 1.757, (19), (312). Single-crystal structure refinement ($R_1 = 0.018$) revealed structure topology typical of the melilite-group minerals, i.e. tetrahedral $[(\text{Al},\text{Mg})(\text{Si}_2\text{O}_7)]$ sheets interleaved with layers of (CaNa) cations. The name reflects the chemical composition of the mineral.

KEYWORDS: alumoåkermanite, åkermanite, melilite, new mineral, volcanic rock, chemical composition, crystal structure, Oldoinyo Lengai, Tanzania.

Introduction

OLDOINYO LENGAI, located in the Gregory Rift in the north of Tanzania, is the only active carbonatite volcano in the world. The volcano is famous for its effusive and highly viscous

natrocarbonatites (*e.g.*, Keller and Krafft, 1990). Nevertheless, the main part of the about 3000 m high cone consists of silicate lavas and pyroclasts (Donaldson *et al.*, 1987; Klaudius and Keller, 2006). Beside phonolites and nephelinites, primitive olivine-melilitites and evolved combeite/melilite-bearing nephelinites play an important role in the evolution of Oldoinyo Lengai.

Melilite occurs in different volcanic rocks at and around Oldoinyo Lengai. It is a major mineral

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in olivine melilitites from the minor volcanic centres Dorobo cone, Lalarasi, Kirurum and Armycon Hill (Dawson *et al.*, 1985; Keller *et al.*, 2006). Melilite in nephelinitic volcanics was reported from the parasitic Nasira cones (Dawson, 1989), from a lava of the 1917 paroxysmal eruption from the main Lengai crater (Keller and Krafft, 1990), but also from an alkalic pyroxenite block from yellow Lengai I phonolitic pyroclasts (Donaldson and Dawson, 1978). Additionally, melilite was described from silicate globules in natrocarbonatite from the 1993 eruption (Dawson *et al.*, 1996; Petibon *et al.*, 1998) and carbonate-silicate lapilli and ashes of both the 1966 and 2007 eruptions (Dawson *et al.*, 1989, 1992; Mitchell and Dawson, 2007).

The melilite from the olivine melilitites exhibits a relatively narrow range in composition. It is åkermanitic with large MgO (8.6–9.9 wt.%), subordinate Al₂O₃ (3.9–5.9 wt.%) and small Na₂O (2.3–3.3 wt.%) and FeO_{total} (2.7–3.7 wt.%). Åkermanite with large MgO and small Na₂O and Al₂O₃ contents (7.0–10.1, 1.3–3.6 and 0–4.2 wt.% respectively) occurs also in carbonate-silicate lapilli and ashes of the 1966 eruption, but it is an Fe-rich variety with 6.7–9.3 wt.% FeO_{total}. Melilite from nephelinites, carbonate-silicate lapilli of the 2007 eruption and some lapilli of the 1966 eruption, as well as silicate globules in natrocarbonatite and alkalic pyroxenite, forms a distinct compositional group – the mineral is a low-Mg variety (3.5–6.0 wt.% MgO), but is enriched in Na₂O (4.9–6.0 wt.%), Al₂O₃ (5.1–8.5 wt.%) and FeO_{total} (5.5–10.9 wt.%). Enrichment of this melilite in Al is so great that some of the analyses show dominance of Al over Mg in the T1 site, e.g. (Ca_{1.52}Na_{0.49})_{Σ2.01}(Al_{0.43}Mg_{0.34}Fe_{0.16}²⁺Fe_{0.06}³⁺)_{Σ0.99}(Si_{1.99}Al_{0.01}O₇) (analysis 3, table 5 in Donaldson and Dawson, 1978) and (Ca_{1.48}Na_{0.53}K_{0.01})_{Σ2.02}(Al_{0.42}Mg_{0.25}Fe_{0.20}²⁺Fe_{0.10}³⁺)_{Σ0.97}(Si_{2.01}O₇) (analysis 8, table 8 in Dawson, 1998). Unfortunately, no other data have been reported for this Na-Al-rich melilite.

In this paper we describe a new mineral from the Oldoinyo Lengai volcano which is a member of the melilite group. The new mineral has been named alumoåkermanite and this name reflects its chemical composition: Ca is the dominant cation in the X site. Aluminium is absent in the T2 site (åkermanite) and the dominance of Al over Mg in the T1 site is indicated by the prefix ‘alumo’. Both the mineral and mineral name have been approved by the Commission on New Mineral and Minerals

Names of the IMA, proposal 2008-049. The cotype specimens are deposited in the Mineralogical Museum, Department of Mineralogy, St. Petersburg State University, St. Petersburg, Russia (sample OL 218, catalogue number 1/19407) and the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia (sample OL 244, catalogue number 3823/1).

Mineral occurrence

Alumoåkermanite was found in a number of volcanic rocks during a systematic mineralogical study of melilite from the Oldoinyo Lengai volcano and surrounding area (Wiedenmann, 2004). The new mineral occurs in evolved olivine-free melilite-nephelinitic ashes and lapilli-tuffs of the 1966/67 and pre-1966 explosive eruptions, in particular, the 1940/1941 ashes, together with nepheline, aegirine-augite but seldom with combeite. Microcrysts of the matrix are nepheline, aegirine-augite, combeite, spinel group minerals and sporadic wollastonite, melinite, titanite and sodalite.

In addition, melilite with a composition intermediate between that of åkermanite and alumoåkermanite has been studied. The melilite occurs as idiomorphic crystals up to 1.5 cm size in unconsolidated ashes within the stratigraphic higher levels of the volcano. These recent ashes and lapilli are classified as combeite-wollastonite-melilite nephelinites.

Physical properties

Alumoåkermanite occurs as tabular phenocrysts (up to 1.5 mm) and microphenocrysts in a fine-grained groundmass (Fig. 1). Macroscopically, the mineral is light brown in colour; it is transparent with a vitreous lustre, and the streak is white. Cleavages or partings are not observed. It is brittle with an uneven fracture. Long- or short-wave ultraviolet radiation produces no observable fluorescence. The measured density, determined by sink-float in heavy liquids for sample OL 244, is 2.96(2) g/cm³, close to the value of 3.00 g/cm³ calculated from average empirical formulae and refined cell dimensions for sample OL 244. The Mohs hardness for OL 244 is ~4.5–5.

Alumoåkermanite is uniaxial (–) with $\omega = 1.635(1)$, $\epsilon = 1.626(1)$ for sample OL 244 and $\omega = 1.635(1)$, $\epsilon = 1.624(2)$ for sample OL 218 (Na

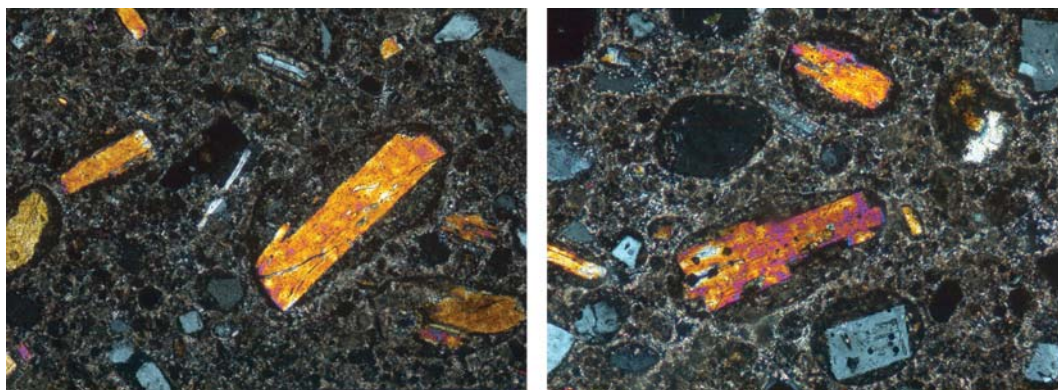


FIG. 1. Tabular crystals of alumoåkermanite (yellow to yellow-orange and orange-red) in nephelinitic ash. Other minerals are nepheline (grey – from dark to light), wollastonite and diopside. Crossed nicols, field of view is 1×0.74 mm. Sample OL 244.

light, 589 nm). In thin section, under cross-polarized light, alumoåkermanite has a yellow to orange-red interference colour; it has straight extinction and positive elongation, and is non-pleochroic.

Melilite of intermediate composition between åkermanite and alumoåkermanite (samples OL mel1 and OL mel2) occurs as idiomorphic crystals up to 1.5 cm size (Fig. 2). Melilite is brown to dark brown in colour, semi-transparent and with a vitreous lustre. The crystals are short, prismatic and tabular with well-developed square {001} faces. The crystals are commonly intergrown, both simply and in a complex fashion. Simple intergrowths preserve the tabular habit of

melilite, while complex intergrowths lead to spherical or star-like shapes (Fig. 2). A micro-indentation (microhardness, VHN load 25 g), test produced a mean = 700 g/mm^2 , in the range $635\text{--}755 \text{ g/mm}^2$ (10 measurements were made on a polished block by C. Stanley, The Natural History Museum, London) which is equivalent to a Mohs hardness of about 5.5–6 for OL mel1 and OL mel2.

Chemical composition

Wavelength-dispersive microprobe analyses of alumoåkermanite were obtained using a Cameca SX100 electron microprobe operated at 15 kV,

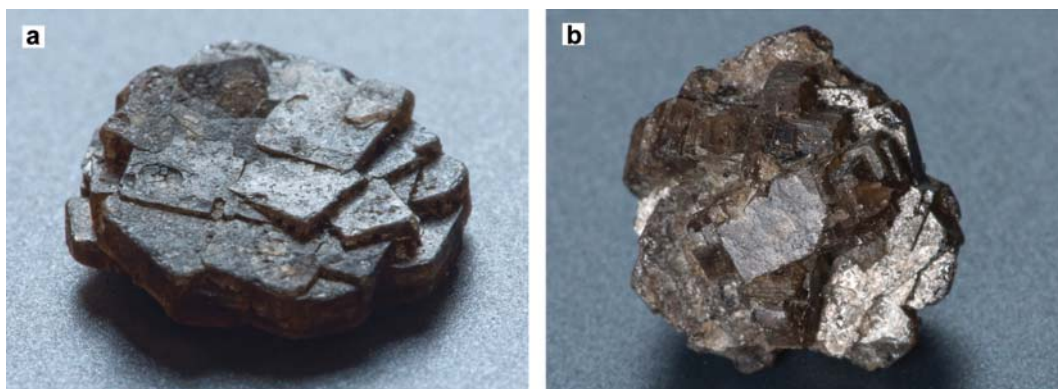


FIG. 2. Intergrown åkermanite-alumoåkermanite crystals (analogues to samples OL mel1 and OL mel2): (a) short-prismatic and tabular habit; (b) complex intergrowth giving a star-like appearance. Size of crystals: 1 cm.

20 nA and a 2 μm final beam diameter (Institut für Geowissenschaften, Universität Freiburg, Germany). The following standard materials were used for calibration: wollastonite (Si, Ca), rutile (Ti), anorthite (Al), fayalite (Fe), rhodonite (Mn), celestine (Sr), albite (Na), orthoclase (K) and MgO (Mg).

The chemical composition of the alumoåkermanite has been studied in samples OL 244, OL 218, OL 194 and OL 8. The mineral is characterized by large amounts of Na_2O (4.6–6.3 wt.%), $\text{FeO}_{\text{total}}$ (4.5–9.6 wt.%) and Al_2O_3

(6.5–9.5 wt.%) and a small amount of MgO (3.0–6.6 wt.%) (Table 1). It also contains minor amounts of SrO (0.6–1.1 wt.%), MnO (0.1–0.3 wt.%) and K_2O (~0.1 wt.%). Calculation of the mineral formulae (Table 1), and particularly the estimation of Fe^{2+} and Fe^{3+} , was based on the procedure described by Droop (1987). Calculations of stoichiometric formulae based on 5 cations and 7 oxygens indicate that FeO is the dominant Fe component in alumoåkermanite, the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio ranging from 0.19 to 0.42 with an average = 0.30..

TABLE 1. Chemical composition (wt.%) of alumoåkermanite from Oldoinyo Lengai.

	— OL 194 —				— OL 244 —				Average	s.d.	OL mel1	OL mel2
SiO_2	43.74	44.17	43.71	43.60	43.94	44.08	42.30	42.93	43.73	0.57	43.12	43.07
TiO_2	0.05	0.02	0.04	n.d.	n.d.	0.05	0.02	n.d.	0.09	0.08	0.05	0.03
Al_2O_3	7.59	8.87	9.01	6.46	8.98	9.51	7.38	9.40	8.32	0.85	7.50	7.42
Fe_2O_3^*	2.74	2.31	3.30	3.90	2.51	1.49	4.28	2.57	2.14		1.82	1.84
FeO^*	3.74	4.82	4.13	5.29	4.65	5.56	5.73	4.00	4.55		4.42	4.48
MnO	0.13	0.19	0.25	0.28	0.19	0.15	0.33	0.20	0.22	0.06	0.16	0.17
MgO	5.35	3.72	3.63	4.55	3.86	3.46	2.98	3.54	4.36	1.17	5.26	5.37
CaO	31.73	29.55	29.38	30.05	29.41	29.54	28.73	28.43	30.24	1.22	30.71	30.69
SrO	0.63	1.07	0.81	n.a.	n.a.	n.a.	1.05	0.78	0.91	0.14	0.59	0.55
Na_2O	5.17	6.20	6.30	5.50	6.28	6.29	5.79	6.34	5.70	0.59	5.09	5.12
K_2O	0.10	0.09	0.13	0.14	0.11	0.08	0.10	0.10	0.10	0.02	0.09	0.10
Total	100.97	101.01	100.69	99.77	99.93	100.21	98.69	98.29	100.34		98.81	98.83
$\text{FeO}_{\text{total}}$	6.21	6.90	7.10	8.80	6.91	6.90	9.58	6.31	6.48	1.24	6.14	6.05
$\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$	0.40	0.30	0.42	0.40	0.33	0.19	0.40	0.37	0.30		0.27	0.27
Si	1.979	1.997	1.982	2.007	1.996	1.998	1.986	1.986	1.991		1.992	1.990
Al	0.021	0.003	0.018	0.000	0.004	0.002	0.014	0.014	0.009		0.008	0.010
Total	2.000	2.000	2.000	2.007	2.000	2.000	2.000	2.000	2.000		2.000	2.000
Al	0.384	0.470	0.464	0.350	0.477	0.506	0.394	0.499	0.438		0.400	0.394
Mg	0.361	0.251	0.245	0.312	0.261	0.234	0.209	0.244	0.296		0.362	0.370
Fe^{2+}	0.142	0.182	0.157	0.204	0.177	0.211	0.225	0.155	0.173		0.171	0.173
Fe^{3+}	0.093	0.079	0.113	0.135	0.086	0.051	0.151	0.089	0.073		0.063	0.064
Mn	0.005	0.007	0.010	0.011	0.007	0.006	0.013	0.008	0.008		0.006	0.007
Ti	0.002	0.001	0.001	n.c.	n.c.	0.002	0.001	n.c.	0.003		0.002	0.001
Total	0.986	0.990	0.990	1.012	1.008	1.009	0.993	0.995	0.992		1.004	1.009
Ca	1.538	1.432	1.428	1.482	1.432	1.434	1.445	1.409	1.475		1.520	1.519
Na	0.454	0.544	0.554	0.491	0.553	0.553	0.527	0.569	0.503		0.456	0.459
Sr	0.017	0.028	0.021	n.c.	n.c.	n.c.	0.029	0.021	0.024		0.016	0.015
K	0.006	0.005	0.008	0.008	0.006	0.005	0.006	0.006	0.006		0.006	0.006
Total	2.014	2.009	2.010	1.981	1.991	1.992	2.007	2.005	2.008		1.998	1.999

* calculated Fe_2O_3 and FeO for samples OL 194, OL 244 and average analysis (Droop, 1987) and calculated from Mössbauer data for samples OL mel1 and OL mel2. Structural formulae based on 5 cations and 7 oxygen (samples OL 194, 244 and average analysis) and on 7 oxygen (samples OL mel1 and OL mel2). Average analysis and standard deviation (s.d.) calculated from 14 individual analyses (8 analyses for Sr). Data for OL mel1 and OL mel2 are average from six analyses per sample. n.d. — not determined. n.a. — not analysed. n.c. — not calculated.

Direct determination of the Fe_2O_3 and FeO content by Mössbauer spectroscopy on melilite crystals from samples OL mel1 and OL mel2 was carried out by C. McCammon (Bayerisches Geoinstitut, Bayreuth). The average analytical microprobe data for both samples are given in Table 1 and the data show an intermediate composition of the mineral between åkermanite and alumoåkermanite – the mineral contains 0.40 a.p.f.u. Al and 0.36 a.p.f.u. Mg (sample OL mel1) and 0.39 a.p.f.u. Al and 0.37 a.p.f.u. Mg (sample OL mel2).

For both samples the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio from Mössbauer spectroscopy is 0.27 ± 0.03 and this ratio gives $\text{Fe}_2\text{O}_3 = 1.82 \text{ wt.}\%$ and $\text{FeO} = 4.42 \text{ wt.}\%$ for the sample OL mel1 and $\text{Fe}_2\text{O}_3 = 1.84 \text{ wt.}\%$ and $\text{FeO} = 4.48 \text{ wt.}\%$ for the sample

OL mel2 (Table 1). The measured value of $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio is quite similar to the calculated $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio for the average analysis of alumoåkermanite.

Data from Table 1 show that the alumoåkermanite contains very little Al in the T2 (Si) site ($<0.02 \text{ a.p.f.u.}$), i.e. the gehlenite end member $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$ is absent in the mineral; all Fe^{3+} is located in the T1 site, as is known for synthetic compounds (Akasaka and Ohashi, 1985; Akasaka *et al.*, 2005). Cations in the X and T1 sites indicate the coupled substitution of $\text{Ca}^{2+} + \text{Mg}^{2+} \rightleftharpoons \text{Na}^+ + \text{Al}^{3+}$, which is common for melilite-group minerals (e.g. Yakubova, 1972; Deer *et al.*, 1997).

Figure 3 shows the composition of the T1 site in the alumoåkermanite. Figure 3b shows the composition in the Al-Mg- Fe^{2+} ternary diagram

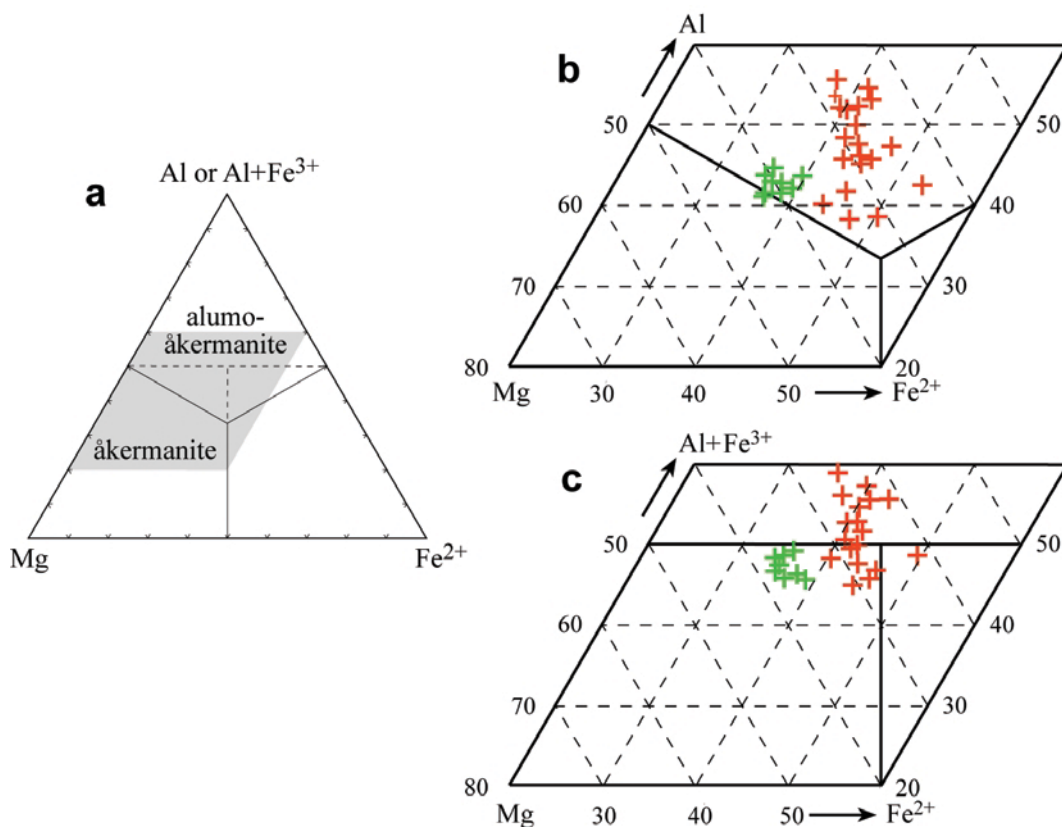


FIG. 3. (a) Composition (T1 site, at.%) of alumoåkermanite from Oldoinyo Lengai. (b) and (c) show the grey shaded area in the triangle. (b) diagram based on the dominant-constituent rule considering Al as the only trivalent cation on the T1 site; and (c) diagram based on the dominant-valency rule considering Al and calculated Fe^{3+} on the T1 site. Dependent on the applied rule, the borderline between åkermanite and alumoåkermanite plots differently. Red crosses – samples OL 244, OL 218, OL 194 and OL 8; green crosses – samples OL mel1 and OL mel2.

based on the dominant-constituent rule, whereas Fig. 3c shows the composition based on the dominant-valency rule of Hatert and Burke (2008). Clearly, there is a fundamental difference between the two classification diagrams. Some of the data points which plot in the alumoåkermanite field on the diagram based on the dominant-constituent rule (Fig. 3b) belong to the åkermanite field on the dominant-valency rule diagram (Fig. 3c). However, both figures indicate that alumoåkermanite is a new mineral species when either of the rules are applied.

Using the Gladstone-Dale constants and the average chemical composition of alumoåkermanite, the calculated compatibility index $[1-(Kp/Kc)] = 0.029$. This value indicates excellent compatibility between the chemical and physical data (with measured density) and $1-(Kp/Kc) = 0.015$ (superior compatibility, with calculated density).

Crystallography

X-ray powder-diffraction data for the alumoåkermanite (sample OL 244), obtained with Stoe Stadi P diffractometer (Cu- $K\alpha_1$ radiation, curved Ge(111) monochromator, 40 kV, 35 mA, transmission geometry, position-sensitive detector, scan width 0.2° , exposure 240 s per scan) (Department of Crystallography, St. Petersburg State University), are given in Table 2. Refined unit-cell parameters from the powder data are $a = 7.7661(4) \text{ \AA}$, $c = 5.0297(4) \text{ \AA}$ and $V = 303.4(1) \text{ \AA}^3$.

Unit-cell parameters of melilite in åkermanite-alumoåkermanite solid solution correlate with mineral composition (Table 3). Parameter a shows a well defined negative correlation with the Al content and parameter c correlates positively with the Na content.

A single crystal of alumoåkermanite from sample OL 244 was mounted on a Stoe IPDS II Image-Plate based X-ray diffractometer operated

TABLE 2. X-ray powder diffraction data for alumoåkermanite.

I/I_o	d_{meas}	I_{calc}	d_{calc}	h	k	l
7	5.501	4	5.491	1	1	0
5	5.038	9	5.030	0	0	1
4	4.226	6	4.222	1	0	1
2	3.885	1	3.883	2	0	0

13	3.712	16	3.709	1	1	1
11	3.476	7	3.473	2	1	0
25	3.075	25	3.074	2	0	1
100	2.859	100	2.858	2	1	1
8	2.747	5	2.746	2	2	0
2	2.5152	2	2.5149	0	0	2
32	2.4563	19	2.4559	3	1	0
10	2.4105	8	2.4100	2	2	1
5	2.3930	8	2.3925	1	0	2
10	2.3021	9	2.3017	3	0	1
3	2.2872	3	2.2865	1	1	2
3	2.2072	2	2.2068	3	1	1
0.5	2.1535	1	2.1539	3	2	0
0.5	2.1110	1	2.1108	2	0	2
8	2.0368	12	2.0369	2	1	2
4	1.9799	3	1.9800	3	2	1
11	1.9413	7	1.9415	4	0	0
8	1.8834	6	1.8836	4	1	0
4	1.8542	4	1.8545	2	2	2
13	1.8303	10	1.8305	3	3	0
1	1.8111	1	1.8113	4	0	1
1	1.8024	1	1.8030	3	0	2
11	1.7634	8	1.7639	4	1	1
19	1.7569	27	1.7570	3	1	2
13	1.7364	8	1.7366	4	2	0
5	1.7201	4	1.7201	3	3	1
1	1.6766	1	1.6766	0	0	3
3	1.6402	1	1.6415	4	2	1
3	1.6395	1	1.6388	1	0	3
3	1.6359	1	1.6359	3	2	2
2	1.6032	3	1.6035	1	1	3
1	1.5390	2	1.5392	2	0	3
1	1.5365	1	1.5368	4	0	2
1	1.5221	1	1.5231	5	1	0
4	1.5095	6	1.5099	2	1	3
1	1.5070	1	1.5076	4	1	2
1	1.4830	1	1.4841	5	0	1
1	1.4802	2	1.4800	3	3	2
4	1.4574	2	1.4577	5	1	1
2	1.4417	1	1.4421	5	2	0
4	1.4302	8	1.4309	2	2	3
2	1.4068	4	1.4072	3	0	3
13	1.3859	12	1.3863	5	2	1
5	1.3726	5	1.3729	4	4	0
2	1.3319	1	1.3319	5	3	0
3	1.3237	2	1.3244	4	4	1
3	1.3237	1	1.3230	3	2	3
2	1.3210	1	1.3215	4	3	2
1	1.3033	1	1.3028	5	1	2
6	1.2940	5	1.2944	6	0	0
1	1.2870	1	1.2875	5	3	1
1	1.2764	1	1.2767	6	1	0
1	1.2683	1	1.2689	4	0	3
1	1.2570	2	1.2574	0	0	4
3	1.2518	4	1.2535	6	0	1
3	1.2518	6	1.2523	4	1	3
1	1.2410	4	1.2413	1	0	4
3	1.2369	3	1.2364	3	3	3

TABLE 3. Comparison of unit-cell parameters for åkermanite–alumoåkermanite solid solution.

	Al (a.p.f.u.)	Na (a.p.f.u.)	<i>a</i> (Å)	<i>c</i> (Å)
Synthetic ¹	0	0	7.845	5.002
Synthetic ²	0	0	7.8345	5.0073
Synthetic ³	0	0	7.8364	5.0101
Åkermanite ⁴	0.06	0.13	7.786	5.018
Åkermanite ⁵	0.08	0.08	7.831	5.009
Åkermanite ⁶	0.07	0.10	7.826	5.004
Synthetic ¹	0.10	0.10	7.820	5.010
Synthetic ¹	0.20	0.20	7.795	5.012
Synthetic ¹	0.30	0.30	7.780	5.020
Åkermanite ⁷	0.30	0.24	7.760	4.998
Åkermanite ⁴	0.35	0.26	7.774	5.014
Åkermanite ⁴	0.37	0.32	7.768	5.014
Synthetic ¹	0.40	0.40	7.755	5.027
Åkermanite ⁸	0.41	0.51	7.760	5.029
Alumoåkermanite ⁹	0.44	0.50	7.7661	5.0297
Synthetic ¹	0.50	0.50	7.740	5.033
Synthetic ⁷	0.50	0.50	7.749	5.032
Synthetic ¹⁰	1	1	7.6344	5.0513

¹ Edgar (1965); ² Hemingway *et al.* (1986); ³ Merlini *et al.* (2006); ⁴ Kukhareno *et al.* (1965);

⁵ Bindi and Bonazzi (2003); ⁶ Bindi and Bonazzi (2005); ⁷ Merlini *et al.* (2008); ⁸ Mokeeva and Makarov (1979);

⁹ this work; ¹⁰ Louisnathan (1970).

at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic Mo-*K*α X-radiation, with frame widths of 2° in ω , and with a 120 s count for each frame. The unit-cell parameters (Table 4) were refined using least-squares techniques. No reflections or diffuse streaks were observed that could be ascribed to the effects of incommensurate modulations (Kusaka *et al.*, 2001; Bindi *et al.*, 2001). The measured intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Stoe program *X-Area*. The *SHELXL* program package was used for all structural calculations (Sheldrick, 1997). For the structure refinement, atomic coordinates were taken from Louisnathan (1970). However, in the crystal studied, the structure has a different absolute configuration that produced a value for the Flack parameter of ~1 (Flack, 1983). Thus, the structure model was inverted in order to obtain the correct absolute configuration. The final model thus included all atomic positional and anisotropic-displacement parameters and a refinable weighting scheme of the structure factors. Occupancies of the Ca and Al sites were calculated using neutral atom scattering curves. The occupancy of the Al site

TABLE 4. Crystallographic data and refinement parameters for alumoåkermanite.

<i>a</i> (Å)	7.7620(7)
<i>c</i> (Å)	5.0311(5)
<i>V</i> (Å ³)	303.12(5)
Space group	<i>P</i> 4 ₂ <i>1m</i>
<i>F</i> ₀₀₀	272
μ (mm ⁻¹)	2.647
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ³)	3.008
Crystal size (mm)	0.22 × 0.14 × 0.12
Radiation	Mo- <i>K</i> α
2θ range, deg.	7.42–58.24
Total Ref.	1952
<i>R</i> _{int}	0.021
Unique Refl.	441
Unique $ F_o = 4\sigma_F$	439
Flack parameter <i>x</i>	-0.05(8)
<i>R</i> ₁	0.018
<i>wR</i> ₂	0.046
<i>S</i>	1.079

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|;$$

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$S = \{ \Sigma [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the number of refined parameters.}$$

was refined using Fe and Al scattering curves. The amount of Mg in the site was calculated based upon obtained site-scattering factor for this position, chemical data and electroneutrality requirements. The final refinement converged to an agreement index (R_1) of 0.018, calculated for the 439 unique reflections with $|F_o| \geq 4\sigma_F$. The final atomic coordinates and anisotropic-displacement parameters are given in Table 5 and selected interatomic distances in Table 6. The complete list of observed and calculated structure factors is deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

The refinement revealed structure topology typical for melilite-group minerals: tetrahedral [(Al,Mg)(Si₂O₇)] sheets interleaved with layers of (CaNa) cations (Smith, 1953; Louisnathan, 1970; Mokeeva and Makarov, 1979; Swainson *et al.*, 1992; Bindi *et al.*, 2001; Bindi and Bonazzi, 2003, 2005). The absence of Al in the silicate tetrahedra is indicated by the average <Si–O> bond length of 1.623 Å, which is typical for pure silicates (Liebau, 1985).

The crystal chemical formula based upon refinement of site-occupation factors can be written as (Ca_{1.5}Na_{0.5})(Al_{0.5}Fe_{0.3}Mg_{0.2})(Si₂O₇) without taking into account variable oxidation state of Fe. This formula is in good agreement with the average empirical formulae of the mineral (Table 1).

Discussion and conclusions

Melilite-group minerals occur in various ultramafic and alkaline rocks, both volcanic and intrusive, and also carbonatites (e.g. Kukharenko *et al.*, 1965; Egorov, 1969, 1991; Watkinson, 1972; Hay, 1978; Nielsen, 1980; Bulakh and Ivanikov, 1984; Rass, 1986; Bell *et al.*, 1996; Dunworth and Wilson, 1998; Ivanikov *et al.*, 1998; de Battistini *et al.*, 2001; Vasilieva and Evdokimov, 2002; Dunworth and Bell, 2003; Chakhmouradian and Zaitsev, 2004; Platz *et al.*, 2004; Keller *et al.*, 2006). Low-Na åkermanite occurs in primitive undifferentiated volcanic rocks (e.g. olivine melilitites) and ultramafic cumulate rocks – olivinites, kugdites and uncomphagrites. Evolved feldspathoid-bearing rocks, such as nephelinites; turjaïtes or okaites contain åkermanite appreciably enriched in both Na and Al. Available data, particularly those melilite-group minerals from Oldoinyo Lengai (Donaldson and

TABLE 5. Atomic coordinates and displacement parameters for alumoåkermanite.

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca*	0.66382(5)	0.83618(5)	0.49132(11)	0.0182(2)	0.0204(2)	$= U_{11}$	0.0138(3)	–0.0016(1)	$= U_{23}$	0.0063(2)
Al**	0	0	0	0.0125(2)	0.0111(3)	$= U_{11}$	0.0154(4)	0	0	0
Si	0.85952(5)	0.64048(5)	0.05699(11)	0.01169(16)	0.0122(2)	$= U_{11}$	0.0106(3)	0.0002(2)	$= U_{23}$	0.0014(2)
O(1)	$\frac{1}{2}$	0	0.8240(6)	0.0237(6)	0.0293(9)	$= U_{11}$	0.0121(1)	0	0	–0.017(1)
O(2)	0.85812(19)	0.64188(19)	0.7411(3)	0.0246(4)	0.0301(6)	$= U_{11}$	0.0136(8)	0.0025(5)	$= U_{23}$	0.0063(9)
O(3)	0.9172(2)	0.81825(18)	0.2026(3)	0.0257(3)	0.0372(8)	0.0186(7)	0.0214(6)	–0.0045(6)	0.0053(6)	–0.0074(6)

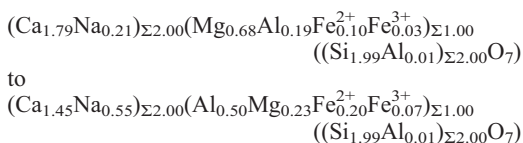
* site-occupation factor = Ca_{0.76}Na_{0.24}

** site-occupation factor = Al_{0.50}Fe_{0.30}Mg_{0.20}

TABLE 6. Selected bond lengths (Å) in the structure of alumoåkermanite.

Ca–O(3)	2.4488(15) 2 ×	Si–O(2)	1.5891(18)
Ca–O(1)	2.457(2)	Si–O(3)	1.6250(14) 2 ×
Ca–O(2)	2.476(2)	Si–O(1)	1.6541(12)
Ca–O(2)	2.6509(15) 2 ×	<Si–O>	1.623
Ca–O(3)	2.7339(17) 2 ×		
<Ca–O>	2.575	Al–O(3)	1.8553(14) 4 ×

Dawson, 1978; Dawson *et al.*, 1985, 1989; Keller and Krafft, 1990; Dawson, 1998; Petitbon *et al.*, 1998; Wiedenmann, 2004; Keller *et al.*, 2006; Mitchell and Dawson, 2007), show a solid solution between åkermanite and alumoåkermanite via substitution $\text{Ca}^{2+} + \text{Mg}^{2+} \rightleftharpoons \text{Na}^+ + \text{Al}^{3+}$ with a range of composition about



Solid solution between åkermanite and alumoåkermanite can be also described using two end members such as $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (åkermanite) and end member $(\text{CaNa})\text{Al}(\text{Si}_2\text{O}_7)$, commonly termed ‘soda melilite’ (a term ‘sodamelilite’ was originally used for the $\text{Na}_2\text{Si}_3\text{O}_7$ end member (Berman, 1929), but later it was re-applied to the compound $(\text{NaCa})\text{Al}(\text{Si}_2\text{O}_7)$ (Berman, 1937; Edgar 1965; Louisnathan, 1970)). Other end members in the åkermanite-alumoåkermanite solid solution are $\text{Ca}_2\text{Fe}^{2+}(\text{Si}_2\text{O}_7)$ and $(\text{CaNa})\text{Fe}^{3+}(\text{Si}_2\text{O}_7)$ components.

Experimental data at $T = 800^\circ\text{C}$ and $P_{\text{H}_2\text{O}} = 1000 \text{ kg/cm}^2$ (0.98 kbar) suggest that the limit of solid solution of the $(\text{NaCa})\text{Al}(\text{Si}_2\text{O}_7)$ component in åkermanite is close to a composition of $(\text{Ca}_{1.4}\text{Na}_{0.6})_{\Sigma 2}(\text{Al}_{0.6}\text{Mg}_{0.4})_{\Sigma 1}(\text{Si}_2\text{O}_7)$ (Edgar, 1965). This synthetic phase is also very close in composition to the alumoåkermanite with the greatest contents of Na_2O and Al_2O_3 from the Oldoinyo Lengai rocks.

The Oldoinyo Lengai volcano is not the only locality for alumoåkermanite. Melilite-group minerals with large contents of both Na_2O and Al_2O_3 are also known from several other localities, including the ultrabasic-alkaline-carbonatite complexes at: Odikhincha (Egorov, 1969, 1991; Rass, 1986), Guly (Rass, 1986) and Turiy Mys (Bulakh and Ivanikov, 1984; Rass, 1986;

Bell *et al.*, 1996; Vasilieva and Evdokimov, 2002; Dunworth and Bell, 2003).

In the Turiy Mys complex, a melilite rich in Na and Al occurs in an intrusive turjaite rock. The microprobe analysis with the greatest Al_2O_3 content gave $\text{SiO}_2 = 44.01$, $\text{Al}_2\text{O}_3 = 9.91$, $\text{Fe}_2\text{O}_{3\text{calc}} = 0.26$, $\text{FeO}_{\text{calc}} = 2.45$, $\text{MnO} = 0.15$, $\text{MgO} = 5.96$, $\text{CaO} = 30.59$, $\text{Na}_2\text{O} = 5.62$, $\text{SrO} = 0.98$, total = 99.93 wt.%. The calculated formula, based on 7 oxygen atoms and a total cation sum = 5, is $(\text{Ca}_{1.48}\text{Na}_{0.49}\text{Sr}_{0.03})_{\Sigma 2.00}(\text{Al}_{0.50}\text{Mg}_{0.40}\text{Fe}_{0.09}^{2+}\text{Fe}_{0.01}^{3+})_{\Sigma 1.00}((\text{Si}_{1.98}\text{Al}_{0.02})_{\Sigma 2.00}\text{O}_7)$. When mineral nomenclature rules are applied, the mineral is clearly alumoåkermanite.

In the Odikhincha complex the melilite rich in Na and Al occurs in a phlogopite-melilite pegmatite. Wet chemical analysis gave $\text{SiO}_2 = 43.50$ wt.%, $\text{Al}_2\text{O}_3 = 9.08$, $\text{Fe}_2\text{O}_3 = 1.31$, $\text{FeO} = 3.09$, $\text{MnO} = 0.12$, $\text{MgO} = 6.31$, $\text{CaO} = 32.49$, $\text{Na}_2\text{O} = 4.21$, $\text{H}_2\text{O}^+ = 0.44$, total = 100.55 wt.% and the formula, based on 7 oxygen atoms, is $(\text{Ca}_{1.57}\text{Na}_{0.37})_{\Sigma 1.94}(\text{Al}_{0.44}\text{Mg}_{0.42}\text{Fe}_{0.12}^{2+}\text{Fe}_{0.04}^{3+})_{\Sigma 1.02}((\text{Si}_{1.96}\text{Al}_{0.04})_{\Sigma 2.00}\text{O}_7)$.

According to the melilite mineral chemistry described here, questions arise as to how the melilite, rich in Na and Al, should be named. The introduction of a new rule in mineral nomenclature, the dominant-valency rule (Hatert and Burke, 2008), leads to a very confusing situation in this and similar cases. If this nomenclature rule is followed, melilite from Odikhincha and Oldoinyo Lengai containing Al as a dominant cation in the T1 site (Fig. 3b,c) must be named åkermanite and its ideal end-member formula is $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$. However, the name åkermanite does not describe the chemical composition of such melilite in an appropriate way. Therefore, we suggest that the so-called dominant-constituent rule is more applicable for nomenclature in the melilite-group.

On the basis of this study and available data for melilite-group minerals (see references above),

we propose the simplified formula for alumoåkermanite to be $(\text{CaNa})_2(\text{Al,Mg,Fe}^{2+})(\text{Si}_2\text{O}_7)$. For the end member ternary diagram, which is commonly used in petrology to describe chemical compositions of the melilite-group minerals, the component $(\text{CaNa})\text{Al}(\text{Si}_2\text{O}_7)$ can be used.

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